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- (54) Abstract Title
Fluorescent conversion filter for an electroluminescent device

(57) A fluorescent converter in filter which converts light in the blue/green wavelength region to light in the red region is provided. The fluorescence conversion filter comprises a fluorescent conversion film 1 which converts the blue/green light (450-520nm) into red light, but does not necessarily absorb all of the blue/green light, and a light absorption film 2 which transmits the red light and absorbs the blue green light. The fluorescent conversion film can be finely patterned and contains a photocuring resin, or a photo- and thermo-curing resin which contains an acrylate polymer, a methacrylate polymer or an acrylate-methacrylate co-polymer as its main component. The filter device may also contain green and red filters 3 and 4.

Figure 1

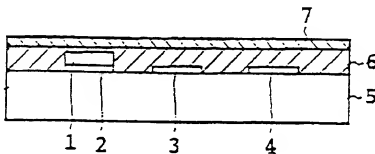


Figure 1

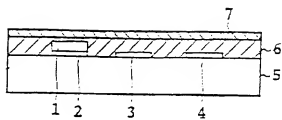


Figure 2

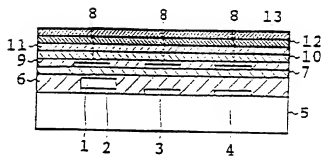
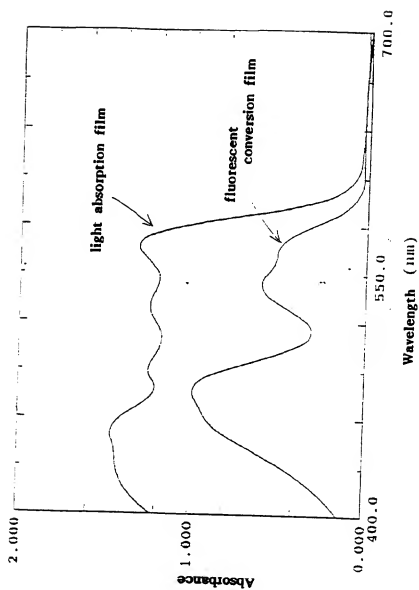


Figure 3



FLUORESCENT CONVERSION FILTER AND
COLOUR DISPLAY DEVICE USING THE SAME

The present invention relates to a fluorescent conversion filter used in combination with a light emitting element in colour display devices for civil or industrial use such as a light-emitting-type multicolour display, a light-emitting-type full-colour display, a colour display panel, a monochromatic signal-light display panel and a back light. The present invention relates also to a colour display device that includes the fluorescent conversion filter. Specifically, the present invention relates to a fluorescent conversion filter that converts light in the region between near ultraviolet and green to light in the red region and facilitates its very fine patterning. Specifically, the present invention relates also to a colour display device that includes the fluorescent conversion filter described above.

Research and development of various light emitting elements have been explored vigorously to meet the increasing demands for flat panel displays for replacing the conventional cathode-ray tubes. The electroluminescent element (hereinafter simply referred to as a "light emitting element") is an all-solid-state self-light-emitting element that meets the above described demands. The electroluminescent element has attracted much attention due to its very high resolution and very high visibility, which other display devices do not exhibit.

To provide a flat panel display with a multicolour display function or a full-colour display function, light emitters of the three primary colours, i.e. red-light emitters, blue-light emitters and green-light emitters, are separately arranged in a matrix and the light emitters are controlled to emit light in the respective colours (cf. Japanese Unexamined Laid Open Patent Applications No. S57-157487, No. S58-147989 and No. H03-214593). It is technically difficult and expensive to use an organic light emitting element for a colour display, since three kinds of light emitting materials for the three primary colours must be arranged very finely in a matrix. In addition, since the lives of the three different light emitting materials are not identical, chromaticity deviations are caused with elapse of time.

The three primary colours are obtained by transmitting the white light from a back light through colour filters (cf. Japanese Unexamined Laid Open Patent Applications No. H01-315988, No. H02-273496 and No. H03-194895). White light with high luminance is necessary to obtain the three primary colours at high luminance. However, any long-life organic light emitting element that emits white light at high luminance has not been obtained so far.

Japanese Unexamined Laid Open Patent Application No. H03-152897 discloses a planar and separate arrangement of fluorescent materials, which absorb the light from a light emitter and emit polychromatic fluorescent light. The planar and separate arrangement of fluorescent materials for emitting polychromatic fluorescent light is applied to the CRT's and the plasma displays. Japanese Unexamined Laid Open Patent Applications No. H03-152897 and H05-258860 disclose a colour conversion method that uses fluorescent materials, which absorb the light from an organic light emitting element and emit fluorescent light in the visible wavelength region. Since the colour of the light that the organic light emitting element emits is not limited to white, an organic light emitting element that emits light at higher luminance may be used as a light source. Japanese Unexamined Laid Open Patent Applications No. H03-152897, No. H08-286033 and H09-208944 disclose a colour conversion method that uses an organic blue-light emitting element as a light source and converts the blue light to green light and red light by respective fluorescent pigments.

By finely patterning the fluorescent conversion films, each including one of those fluorescent pigments, a full-colour light-emitting type display may be constructed even when a weak energy ray such as a near ultraviolet ray and a visible ray from a light emitter is used. The fluorescent conversion filter is patterned, in the similar manner as the inorganic fluorescent converter, by dispersing a fluorescent pigment into liquid photoresist (photo-reactive polymer), forming a film of the dispersion liquid by spin coating and by patterning the formed film by the photolithographic technique (cf. Japanese Unexamined Laid Open Patent Applications No. H05-198921 and No. H05-258860). The fluorescent conversion filter is patterned also by dispersing a fluorescent pigment into a basic binder and by etching the basic binder film including the

fluorescent pigment with acidic aqueous solution (cf. Japanese Unexamined Laid Open Patent Application No. H09-208944).

The liquid photoresist, into that an organic fluorescent pigment is dispersed, includes a photo-polymerization agent or a thermosetting agent (polymerization initiator), reactive multifunctional monomers and reactive multifunctional oligomers. During the photolithographic process for patterning, bleaching of the organic pigment and extinction are often caused by the radicals and ions produced from the photo-polymerization agent or thermosetting agent (polymerization initiator), reactive multifunctional monomers and reactive multifunctional oligomers.

Since a photoresist is coated on a fluorescent conversion film including a basic binder and the photoresist is patterned before the etching with acidic aqueous solution, defects in the photoresist adversely affect the fluorescent conversion film. This problem has not been obviated yet.

For obtaining red light with high colour purity from the blue or green light by the foregoing colour conversion method, it is necessary for the absorbance of the conventional mono-layered red colour filter to be more than 1 in the wavelength region between 450 nm and 520 nm. When the absorbance of the fluorescent conversion film is less than 1, more than 10 % of the light from the blue- or green-light emitting element is not absorbed and highly pure red light is not obtained. Therefore, the pigment concentration in the red colour filter or the thickness of the red colour filter should be increased so that the absorbance of the red colour filter may be more than 1.

Generally, the fluorescent pigment added to much causes self-absorption and concentration extinction. Due to these adverse effects, a high conversion efficiency is not obtained when the pigment concentration in the red colour filter is high enough to obtain the absorbance of more than 1 in the wavelength region between 450 nm and 520 nm, although highly pure red light may be obtained. Alternatively, the fluorescent pigment concentration is reduced and the thickness of the colour conversion filter is increased so that the absorbance of more than 1 may be obtained in the wavelength region between 450 nm and 520 nm. However, the thickened colour conversion filter causes light leakage to the adjacent pixels, resulting in a narrowed angle of visibility.

In manufacturing the displays of colour conversion type, the distance between the fluorescent conversion filter and the organic electroluminescent (EL) element should be carefully adjusted. When the distance between the fluorescent conversion filter and the organic EL element is long, the light leaks to the adjacent pixels, resulting in an narrowed angle of visibility. In other words, as the distance between the fluorescent conversion filter and the organic EL element is shorter, the angle of visibility is wider. Therefore, it is desirable to form an organic EL layer in contact with the upper surface of a colour conversion filter.

Japanese Unexamined Laid Open Patent Application No. H08-279394 discloses a method for forming a transparent and electrically insulative inorganic layer directly onto fluorescent layers at first. However, it is difficult to flatten the colour steps on the fluorescent conversion filter and concave and convex portions are caused on the as-formed electrically insulative inorganic layer. Therefore, the organic light emitting element is inevitably formed on the concave and convex portions, causing unfavourable influences to obtaining very fine display performances.

To obviate the problem described above, a protection layer is coated on the fluorescent conversion filter to flatten the surface on which the electrically insulative inorganic oxide layer is formed. However, since the thickness of the protection layer changes with the thickness of the fluorescent conversion films, the protection layer for flattening a thick fluorescent conversion film is inevitably thick. The thick protection film narrows the angle of visibility of the light emitting element formed on the protection film.

According to the method described above, the fluorescent conversion films are heated repeatedly during hardening the protection layer. When the glass transition temperature of the fluorescent conversion film is low, pattern distortions are caused due to the difference of the linear expansion coefficients of the fluorescent conversion film and the protection film. To obviate this problem, protection layer materials, which harden at a low temperature, harden by the ultraviolet light or harden by the visible light, should be selected. However, even when the fluorescent conversion filter free from pattern distortions is manufactured by using the materials selected according to

the above guideline, pattern distortion is caused in the fluorescent conversion filter, whose glass transition temperature is low, by a high temperature test.

In view of the foregoing, it is an object of the invention to provide a fluorescent conversion filter including a fluorescent conversion film that converts the light in the region between near ultraviolet and green to the light in the red region. It is another object of the invention to provide a fluorescent conversion filter including a fluorescent conversion film that facilitates its fine patterning. It is still another object of the invention to provide a fluorescent conversion filter including a fluorescent conversion film that exhibits excellent display performances. It is a further object of the invention to provide a display device including such an excellent fluorescent conversion filter.

The foregoing problems are obviated by laminating a light absorption film, the absorbance of which is more than 1 in the wavelength region between 450 nm and 520 nm on the display plane side of a fluorescent conversion film, the absorbance of which is 1 or less in the wavelength region between 450 nm and 520 nm. A fluorescent filter that can be patterned very finely is obtained especially when the fluorescent conversion film contains a photo-curing resin or a photo- and thermo-setting resin that contains an acrylate resin and/or a methacrylate resin, and a copolymer of the acrylate polymer and the methacrylate polymer as its main components.

Therefore, according to an aspect of the invention, there is provided a fluorescent conversion filter for displaying colours cooperatively with a light emitting element, the fluorescent conversion filter including: a fluorescent conversion film; and a light absorption film laminated on the fluorescent conversion film on the side of the display plane of the fluorescent conversion film; the fluorescent conversion film converting light in the region between near ultraviolet and green to light in the red region; the fluorescent conversion film facilitates its very fine patterning; the light absorbance of the fluorescent conversion film is 1 or less in the wavelength region between 450 nm and 520 nm; the light absorbance of the light absorption film is more than 1 in the wavelength region between 450 nm and 520 nm.

Advantageously, the matrix resin of the fluorescent conversion film is a photo-curing resin or a photo- and thermo-setting resin.

Advantageously, the photo-curing resin or the photo- and thermo-setting resin contains an acrylate polymer, a methacrylate polymer or an acrylate-methacrylate copolymer as its main component.

According to another aspect of the invention, there is provided a colour display device that includes the fluorescent conversion filter described above.

The invention can be performed in various ways and some embodiments will now be described by way of example and with reference to the accompanying drawings, in which:

Figure 1 is a cross section of a fluorescent conversion filter according to a first embodiment of the invention;

Figure 2 is a cross section of a colour display device that uses the fluorescent conversion filter of Figure 1; and

Figure 3 is a graph showing the absorption curves of the light absorption film and the fluorescent conversion film constituting the fluorescent conversion filter according to the first embodiment of the invention.

Referring now to Figure 1, the fluorescent conversion filter of the invention includes a fluorescent conversion film 1, a light absorption film 2, a green colour filter 3 and a blue colour filter 4 on a glass substrate 5 that works as a display plane, a protection layer 6 for flattening the upper surface of the laminate and an insulative inorganic oxide film 7 on the flat upper surface. The absorbance of the fluorescent conversion film 1 is 1 or less in the wavelength region between 450 nm and 520 nm. The absorbance of the light absorption film 2 is more than 1 in the wavelength region between 450 nm and 520 nm. The light absorption film 2 is laminated on the display plane side of the fluorescent conversion film 1.

By laminating the light absorption film 2, the absorbance of which is more than 1 in the wavelength region between 450 nm and 520 nm, on the display plane side of the fluorescent conversion film 1, the absorbance of which is 1 or less in the wavelength region between 450 nm and 520 nm, the leakage light in the wavelength region between 450 nm and

520 nm is interrupted. Due to this, a fluorescent conversion filter is realized that prevents the conversion efficiency lowering, caused by the concentration extinction and such causes, in the thickness range (preferably less than $20\mu\text{m}$) of the fluorescent conversion filter for maintaining the angle of visibility determined by the thickness of the fluorescent conversion film or the protection layer.

The fluorescent conversion filter of the invention is applicable to a monochromatic or dichromatic signal light display device. In such a case, either one or both of the green colour filter and the blue colour filter are omitted from the constituent elements.

By using a photo-curing resin or a photo- and thermo-setting resin, that contains an acrylate polymer, a methacrylate polymer or an acrylate-methacrylate copolymer as its main components, in the fluorescent conversion film, the fluorescent conversion film can be patterned by the conventional photolithographic technique. Therefore, very fine patterning is realized easily with low costs. And, since the glass transition temperature of the fluorescent conversion filter that employs such the fluorescent conversion film is high, the fluorescent conversion filter of the invention realizes practically sufficient endurance against subsequent processes and thermal resistance.

The colour display device according to the invention includes the foregoing fluorescent conversion filter combined with a light emitting element. The colour display device exemplary shown in Figure 2 includes layers constituting a light emitting element and laminated one by one on an insulative inorganic oxide film 7 of the fluorescent conversion filter exemplary shown in Figure 1. More in detail, a patterned transparent electrode 8 is laminated on the insulative inorganic oxide film 7. A hole injection layer 9 is laminated on the patterned transparent electrode 8, a hole transport layer 10 on the hole injection layer 9, an organic light emitting layer 11 on the hole transport layer 10, an electron injection layer 12 on the organic light emitting layer 11 and an electrode 13 on the electron injection layer 12.

Now the fluorescent pigments used for the fluorescent conversion film of the fluorescent conversion filter will be explained.

The fluorescent pigments, which absorb the light in the blue region or in the bluish green region from a light emitting element and convert the absorbed light to the light in the red region, includes the Rhodamine pigments such as Rhodamine B, Rhodamine 6G, Rhodamine 3B, Rhodamine 101, Rhodamine 110, Sulforhodamine, Basic violet 11 and Basic red 2, the cyanine pigments such as 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyrene (DCM), the pyridine pigments such as 1-ethyl-2-[4-(p-dimethylaminophenyl)-1, 3-butadienyl]-pyridium-perchlorate (Pyridine 1) and the oxazine pigments. In addition, various dyes including the direct dyes, acidic dyes, basic dyes and disperse dyes are used as far as they are fluorescent.

The fluorescent pigments which convert the absorbed light in the blue region or in the bluish green region to the light in the wavelength region other than red are also employable as described later. The fluorescent pigments which convert the light in the blue region or in the bluish green region to the light in the green region includes the coumarin pigments such as 3-(2'-benzothiazolyl)-7-diethylaminocoumarin (Coumarin 6), 3-(2'-benzoimidazolyl)-7-N,N-diethylaminocoumarin (Coumarin 7), 3-(2'-N-methylbenzoimidazolyl)-7-N,N-diethylaminocoumarin (Coumarin 30) and 2,3,5,6-1H,4H-tetrahydro-8-trifluoromethylquinolizine (9,9a,1-gh)coumarin (Coumarin 153), the coumarin dyes such as Basic yellow 51, and the naphthalimide pigments such as Solvent yellow 11 and Solvent yellow 116. In addition, various dyes including the direct dyes, acidic dyes, basic dyes and disperse dyes are used as far as they are fluorescent.

It is preferable for the fluorescent conversion film to contain one or more fluorescent pigments or one or more fluorescent dyes which emit fluorescent light in the red region. One or more fluorescent pigments or one or more fluorescent dyes which emit fluorescent light in the green region may be combined with the one or more fluorescent pigments or fluorescent dyes which emit fluorescent light in the red region. It is more preferable for the fluorescent conversion film to contain one or more fluorescent pigments which emit fluorescent light in the red region and one or more fluorescent pigments which emit fluorescent light in the green region.

The above described pigments which emit the fluorescent light in the red or green region may be masticated previously in polymethacrylate, poly(vinyl chloride), vinyl chloride-vinyl acetate copolymer resin, alkyd resin, aromatic sulfonamide resin, urea resin, melamine resin, benzoguanamine resin and their appropriate mixture. These pigments are used alone or in an appropriate combination.

The pigment concentration in the fluorescent conversion film is set in the range that does not cause concentration extinction nor self-absorption. Preferably, the fluorescent conversion film is less than $20\mu\text{m}$ in thickness and its absorbance is from 0.1 to 1 in the wavelength region between 450 nm and 520 nm. When the absorbance is less than 0.1, the fluorescent conversion film cannot convert the light emitted from the light emitting element effectively to red light. When the absorbance is more than 1, concentration extinction or self-absorption is caused, resulting in a low conversion efficiency.

The photo-curing resin or the photo- and thermo-setting resin used in the fluorescent conversion film according to the invention is a polymerization product or a cross-linking product polymerized or cross-linked through the radicals and ions produced by an optical or thermal treatment so that the resin may be insoluble and may not melt easily.

More in detail, the foregoing photo-curing resin or photo- and thermo-setting resin is

(1) a polymerization product of acrylic multifunctional monomers and acrylic multifunctional oligomers polymerized through photo-radicals or thermo-radicals produced by an optical or thermal treatment from a composition, including the acrylic multifunctional monomers, the acrylic multifunctional oligomers and an optical or thermal polymerization initiator,

(2) a cross-linking product of poly (vinyl cinnamate) cross-linked by dimerizing a composition including poly (vinyl cinnamate) and a sensitizer by an optical or thermal treatment,

(3) a cross-linking product of the composition, including linear or cyclic olefin and bisazido, cross-linked with olefin through nitrene produced from a composition by an optical or thermal treatment, or

(4) a polymerization product of monomers having an epoxy radical polymerized through the acid (cations) produced from a composition including the monomers and optical acid generating agent by an optical or thermal treatment.

The fluorescent conversion film that emits fluorescent light in the red region includes the foregoing fluorescent pigment, and the polymer of the foregoing photo-curing resin or the photo- and thermo-setting resin. Among the photo-curing resins or the photo- and thermo-setting resins, the polymerization product (1) of acrylic multifunctional monomers and oligomers, which include a plurality of acryloyl groups or methacryloyl groups, polymerized through the photo-radicals or thermo-radicals produced from the composition, including the acrylic multifunctional monomers, the acrylic multifunctional oligomers and an optical or thermal polymerization initiator, by an optical or thermal treatment, is preferable, since the polymerization product (1) can be patterned finely and exhibit high solvent resistance and thermal resistance.

The light absorption film is formed on a transparent substrate by printing, dispersing, dyeing, electro-deposition or micelle-electrolysis. Various conventional pigments and dyes are used for the light absorption film.

A red filter material (Color Mosaic CR-7001 supplied from FUJIFILM OLIN CO., LTD.) is coated by spin-coating on a glass substrate 5 (143X112X1.1 mm³, supplied from CORNING INC.) and the coated filter material layer is patterned by the photolithographic method, resulting in a red filter layer (light absorption film 2) consisting of stripes, 1 μ m in thickness, 0.33 mm in width and spaced apart for 1.2 mm. As shown in Figure 3, the absorbance of the light absorption film 2 is more than 1 in the wavelength region between 450 nm and 520 nm.

A blue filter material (Color Mosaic CB-7001 supplied from FUJIFILM OLIN CO., LTD.) and a green filter material (Color Mosaic CG-7001 supplied from FUJIFILM OLIN CO., LTD.) are coated by spin-coating on the substrate 5. Then, the coated filter material layers are patterned by the photolithographic method, resulting in a blue colour filter 4 and a green

colour filter 3, each consisting of stripes, $1\mu\text{m}$ in thickness, 0.33 mm in width and spaced apart for 1.2 mm .

A fluorescent conversion film 1 is formed on the light absorption film 2 by spin-coating a transparent photo-polymerizing resin (SP-2600 supplied from Showa Highpolymer Co., Ltd.) containing Coumarin 6, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film 1 through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm , and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate in an oven, a fluorescent conversion filter of $7\mu\text{m}$ in thickness consisting of the light absorption film 2 of $1\mu\text{m}$ in thickness and the fluorescent conversion film 1 of $6\mu\text{m}$ in thickness is obtained. As shown in Figure 3, the pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film 1 at the film thickness of $6\mu\text{m}$ is 1 or less, in the wavelength region between 450 nm and 520 nm .

The glass transition temperature of the fluorescent conversion filter according to the first embodiment, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 112°C .

A protection layer 6 is formed on the so-far-laminated fluorescent conversion filter by spin-coating a UV-curing resin (epoxy-modified acrylate) and by irradiating the light from a high pressure mercury lamp to the coated UV-curing resin. The thickness of the protection layer 6 is $3\mu\text{m}$ above the fluorescent conversion film 1.

The formation of the protection layer 6 does not cause any pattern distortion in the fluorescent conversion filter and the protection layer 6 remains flat. Any distortion is not caused in the fluorescent conversion filter and the protection layer by the high temperature test conducted at 100°C . An insulative inorganic oxide film 7 is formed on the protection layer 6 by sputtering.

Figure 2 is a cross section of a colour display device that uses the fluorescent conversion filter of Figure 1. Referring now to Figure 2, the colour display device includes an organic light emitting element on

the upper surface of an fluorescent conversion filter. The organic light emitting element consists of six layers: a transparent electrode as an anode, a hole injection layer, a hole transport layer, an organic light emitting layer, an electron injection layer and an electrode as a cathode.

At first, a transparent electrode (hereinafter sometimes referred to as an "ITO") 8 is deposited on the entire upper surface of the insulative inorganic oxide film 7 of the fluorescent conversion filter. A photoresist agent (OFRP-800 supplied from Tokyo Ohka Kogyo Co., Ltd.) is coated on the ITO and patterned by photolithography. A stripe pattern of the ITO consisting of stripes, 0.33 mm in width, 100 nm in thickness and spaced apart for 0.07 mm, is formed.

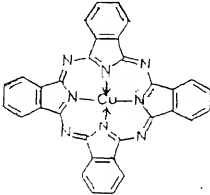
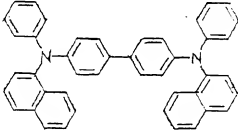
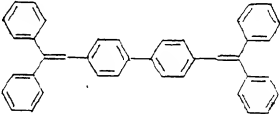
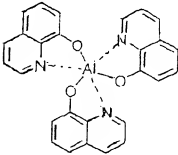
Then, the laminate, including the substrate, the fluorescent conversion filter and the transparent electrode is loaded into a resistance heating vacuum deposition chamber, and a hole injection layer 9, a hole transport layer 10, an organic light emitting layer 11 and an electron injection layer 12 are deposited one by one without breaking the vacuum. Table 1 lists the structural formula of the materials used for these organic layers. During the film desposition, the vacuum chamber is evacuated to 1×10^{-4} Pa. A copper phthalocyanine (CuPc) layer of 100 nm in thickness is deposited for the hole injection layer 9. A 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl (α -NPD) layer of 20 nm in thickness is deposited for the hole transport layer 10. A 4,4'-bis(2,2'-diphenylvinyl)biphenyl (DPVBi) layer of 30 nm in thickness is deposited for the organic light emitting layer 11. And, an aluminium chelate (Alq) layer of 20 nm in thickness is deposited for the electron injection layer 12.

Then, the substrate with the organic layers deposited thereon is taken out from the vacuum deposition chamber and a mask for obtaining the stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 0.07 mm, is positioned perpendicularly to the ITO stripes. The substrate carrying the mask is loaded again into the resistance heating vacuum deposition chamber and a Mg/Ag (10:1 in weight ratio) layer of 200 nm in thickness is deposited for the electrode 13 as a cathode.

The foregoing transparent electrode 8, hole injection layer 9, hole transport layer 10, organic light emitting layer 11, electron injection layer 12 and electrode 13 constitute an organic light emitting element.

The colour display device including the fluorescent conversion filter and the organic light emitting element is sealed with a sealant glass and a UV-curing adhesive in a dry nitrogen atmosphere in a glove box.

Table 1

Layers and Materials	Structural formulas
Hole injection layer 9 CuPc	
Hole transport layer 10 α -NPD	
Light emitting layer 11 DPVBi	
Electron injection layer 12 Alq	

In the similar way as in the first embodiment, a fluorescent conversion film 1 is formed on a light absorption film 2 by spin-coating a transparent photo-polymerizing resin (SP-1509 supplied from Showa Highpolymer Co., Ltd.) containing Coumarin 7, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film 1 through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate in an oven, a fluorescent conversion filter of $7\mu\text{m}$ in thickness consisting of the light absorption film 2 of $1\mu\text{m}$ in thickness and the fluorescent conversion film 1 of $6\mu\text{m}$ in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film 1 at the film thickness of $6\mu\text{m}$ is 1 or less in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the second embodiment, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 117°C .

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

In the similar way as in the first embodiment, a fluorescent conversion film 1 is formed on a light absorption film 2 by spin-coating a transparent photo-polymerizing resin (V-2400PET Series supplied from Nippon Steel Chemical Co., Ltd.) containing Coumarin 7, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film 1 through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate by

heating, a fluorescent conversion filter of $7\mu\text{m}$ in thickness consisting of the light absorption film 2 of $1\mu\text{m}$ in thickness and the fluorescent conversion film 1 of $6\mu\text{m}$ in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film 1 at the film thickness of $6\mu\text{m}$ is 1 or less in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the third embodiment, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 170°C .

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

In the similar way as in the first embodiment, a fluorescent conversion film 1 is formed on a light absorption film 2 by spin-coating a mixture of transparent photo-polymerizing resin (V-2400PET Series supplied from Nippon Steel Chemical Co., Ltd.) and additional transparent photo-polymerizing resin (V-2400PET Series supplied from Nippon Steel Chemical Co., Ltd.) containing Coumarin 7, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin mixture in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film 1 through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate in an oven, a fluorescent conversion filter of $7\mu\text{m}$ in thickness consisting of the light absorption film 2 of $1\mu\text{m}$ in thickness and the fluorescent conversion film 1 of $6\mu\text{m}$ in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film 1 at the film thickness of $6\mu\text{m}$ is 1 or less in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the fourth embodiment, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 220°C .

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

A fluorescent conversion film is formed on a glass substrate 5 (143X112X1.1 mm³, supplied from CORNING INC.) by spin-coating a transparent photo-polymerizing resin (SP-2600 supplied from Showa Highpolymer Co., Ltd.) containing Coumarin 6, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained fluorescent conversion film in an oven, a fluorescent conversion filter of 25 μ m in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film at the film thickness of 25 μ m is more than 2 in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the comparative example 1, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 140°C.

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the comparative fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

A red filter material (Color Mosaic CR-7001 supplied from FUJIFILM OLIN CO., LTD.) is coated by spin-coating on a glass substrate 5 (143X112X1.1 mm³, supplied from CORNING INC.) and the coated filter material layer is patterned by the photolithographic method, resulting in a red filter layer (light absorption film 2) consisting of stripes, 0.5 μ m in thickness, 0.33 mm in width and spaced apart for 1.2 mm. The absorbance of the light absorption film 2 is less than 1 in the wavelength

region between 450 nm and 520 nm. A blue colour filter and a green colour filter are formed in the same way as in the first embodiment.

A fluorescent conversion film 1 is formed on the light absorption film 2 by spin-coating a transparent photo-polymerizing resin (SP-2600 supplied from Showa Highpolymer Co., Ltd.) containing Coumarin 6, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven at 80°C. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film 1 through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate in an oven, a fluorescent conversion filter of 15.5 μ m in thickness consisting of the light absorption film 2 of 0.5 μ m in thickness and the fluorescent conversion film 1 of 15 μ m in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film 1 at the film thickness of 15 μ m is more than 1.5 in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the comparative example 2, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 140°C.

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the comparative fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

A fluorescent conversion film is formed on a glass substrate 5 (143X112X1.1 mm³, supplied from CORNING INC.) by spin-coating a transparent photo-polymerizing resin (SP-2600 supplied from Showa Highpolymer Co., Ltd.) containing Coumarin 6, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film 1 is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and

spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained fluorescent conversion film in an oven, a fluorescent conversion filter of $7\mu\text{m}$ in thickness is obtained. The pigment concentration in the fluorescent conversion film is adjusted such that the absorbance of the fluorescent conversion film at the film thickness of $7\mu\text{m}$ is more than 2 in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the comparative example 3, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 140°C .

An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the comparative fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

A red filter material (Color Mosaic CR-7001 supplied from FUJIFILM OLIN CO., LTD..) is coated by spin-coating on a glass substrate 5 ($143\text{X}112\text{X}1.1\text{ mm}^3$, supplied from CORNING INC.) and the coated filter material layer is patterned by the photolithographic method, resulting in a red filter layer (light absorption film 2) consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm. Then, a fluorescent conversion film is formed on the light absorption film 2 by spin-coating a transparent photo-polymerizing resin (SR235 supplied from NIPPON KAYAKU CO., LTD.) containing Coumarin 7, Rhodamine 6G and Basic violet 11 and by drying the coated transparent photo-polymerizing resin in an oven. Then, the fluorescent conversion film is patterned by the contact exposure technique that exposes the light from a high pressure mercury lamp to the fluorescent conversion film through a mask for obtaining a stripe pattern consisting of stripes, 0.33 mm in width and spaced apart for 1.2 mm, and by developing the exposed stripe pattern with alkaline aqueous solution. Then, by drying the obtained laminate in an oven, a fluorescent conversion filter of $7\mu\text{m}$ in thickness is obtained. The absorbance of the fluorescent conversion film at the film thickness of $6\mu\text{m}$ is less than 1 in the wavelength region between 450 nm and 520 nm.

The glass transition temperature of the fluorescent conversion filter according to the comparative example 4, measured in a differential scanning calorimeter (DSC supplied from RIGAKU CORPORATION), is 60°C.

A protection layer is formed on the so-far-laminated comparative fluorescent conversion filter in the same way as in the first embodiment. Concave and convex portions are caused on the protection layer due to the pattern distortion of the fluorescent conversion filter. An organic light emitting element is formed on the fluorescent conversion filter in the same way as in the first embodiment.

A colour display device including the fluorescent conversion filter and the light emitting element is sealed in the same way as in the first embodiment.

Table 2 lists the evaluation results of the colour conversion filters according to the first through fourth embodiments and comparative examples 1 through 4. The evaluation items and the evaluation methods will be described later.

Table 2

	Chromaticity		Film thickness	Angle of visibility	Luminance	Endurance against subsequent processes
	x	y				
E 1	0.65	0.34	7 μ m	Within \pm 80°	1	O
E 2	0.64	0.33	7 μ m	Within \pm 80°	1.04	O
E 3	0.65	0.34	7 μ m	Within \pm 80°	0.98	O
E 4	0.65	0.33	7 μ m	Within \pm 80°	1.05	O
C 1	0.64	0.33	25 μ m	Within \pm 30°	0.98	O
C 2	0.65	0.34	15.5 μ m	Within \pm 50°	1.05	O
C 3	0.64	0.35	7 μ m	Within \pm 80°	0.60	O
C 4	0.65	0.35	7 μ m	Within \pm 80°	0.89	X

The CIE chromaticity coordinates are measured with a photometric system (MCPD-1000 supplied from Otsuka Electronics Co., Ltd.). The angles of visibility are measured at every 5 degrees of angle from 0°, defined as the angle at that the light receiving portion of the photometric system is perpendicular to the glass substrate of the specimen, to the right and left sides within the range of \pm 80 degrees of angle.

The step heights from the glass substrate surface of the light absorption film, the fluorescent conversion film and the fluorescent conversion filters including the light absorption film and the fluorescent conversion film are measured with a surface roughness meter (DEKTA II A supplied from ULVAC JAPAN Ltd.).

A reference voltage is defined as the voltage at that the luminance of the light emitted from the organic light emitting element through the fluorescent conversion filter of the first embodiment is 50 cd/m^2 . The relative conversion efficiencies are evaluated by comparing the luminance values measured by applying the reference voltage to the organic light emitting elements on the respective fluorescent filters with 50 cd/m^2 .

The endurance of the fluorescent conversion filters against subsequent processes are examined in terms of defects such as open circuits and short circuits caused by making the light emitting elements on the respective fluorescent conversion filters emit light.

The colour display device including a light emitting element on either one of the respective fluorescent conversion filters according to the first through fourth embodiments is a very fine and very practical display device that emits red light with a high colour purity, and exhibits a wide angle of visibility and high endurance against subsequent manufacturing processes.

The evaluation results of the fluorescent conversion filters according to the comparative examples 1 through 4 will be described below.

Since the fluorescent conversion film according to the comparative example 1 is as thick as $25\mu\text{m}$, the optical path between the organic light emitting element and the fluorescent conversion filter is long. The CIE chromaticity coordinate changes when the angle of visibility is outside $\pm 30^\circ$ due to the long optical path length and the red colour purity is deteriorated.

Since the fluorescent conversion film according to the comparative example 2 is as thick as $15\mu\text{m}$ due to its low absorbance, the optical path between the organic light emitting element and the fluorescent conversion filter is long. The CIE chromaticity coordinate changes when the angle of visibility is outside $\pm 50^\circ$ due to the long optical path length and the red colour purity is deteriorated.

The relative luminance of the light emitted through the fluorescent conversion filter according to the comparative example 3 is 0.60 with respect to the light emitted through the fluorescent conversion filter according to the first embodiment at the same voltage applied to the respective light emitting elements. The low luminance according to the comparative example 3 is attributed to the low colour conversion efficiency due to the extinction and self absorption caused by the pigment concentration, that is adjusted such that the absorbance in the wavelength region between 450 nm and 520 nm is more than 2 at the film thickness of 7 μ m.

Some scattered non-light-emitting portions and, therefore, uneven light emission are caused in the organic light emitting element on the fluorescent conversion filter according to the comparative example 4. Due to the concave and convex portions on the protection layer, open circuits, which are very hazardous for highly fine display, are caused in the display device.

As explained above, the fluorescent conversion filter according to the invention facilitates converting the light in the wavelength region between near ultraviolet and green to the light in the red region, can be finely patterned and exhibits excellent display performances. The fluorescent conversion filter according to the invention is preferably applicable to the colour display devices for civil or industrial use such as a light-emitting-type multicolour display, a light-emitting-type full-colour display, a colour display panel, a monochromatic signal-light display panel and a back light. The fluorescent conversion filter according to the invention facilitates manufacturing the colour display devices easily with low manufacturing costs.

CLAIMS

1. A fluorescent conversion filter for displaying colours cooperatively with a light emitting element, the fluorescent conversion filter comprising:

a fluorescent conversion film converting light in the region between near ultraviolet and green to light in the red region and facilitating very fine patterning thereof;

a light absorption film laminated on the fluorescent conversion film on the side of the display plane of the fluorescent conversion film; wherein

the light absorbance of the fluorescent conversion film is 1 or less in the wavelength region between 450 nm and 520 nm;

the light absorbance of the light absorption film is more than 1 in the wavelength region between 450 nm and 520 nm.

2. The fluorescent conversion filter according to Claim 1, wherein the fluorescent conversion film comprises a photo-curing resin as the matrix resin thereof.

3. The fluorescent conversion filter according to Claim 1, wherein the fluorescent conversion film comprises a photo- and thermo-setting resin as the matrix resin thereof.

4. The fluorescent conversion filter according to Claim 2, wherein the photo-curing resin contains an acrylate polymer as the main component thereof.

5. The fluorescent conversion filter according to Claim 2, wherein the photo-curing resin contains a methacrylate polymer as the main component thereof.

6. The fluorescent conversion filter according to Claim 2, wherein the photo-curing resin contains an acrylate-methacrylate copolymer as the main component thereof.

7. The fluorescent conversion filter according to Claim 3, wherein the photo- and thermo-setting resin contains an acrylate polymer as the main component thereof.

8. The fluorescent conversion filter according to Claim 3, wherein the photo- and thermo-setting resin contains a methacrylate polymer as the main component thereof.

9. The fluorescent conversion filter according to Claim 3, wherein the photo- and thermo-setting resin contains an acrylate-methacrylate copolymer as the main component thereof.
10. A colour display device comprising:
 - a light emitting element, and a fluorescent conversion filter including a fluorescent conversion film converting light in the region between near ultraviolet and green to light in the red region and facilitating very fine patterning thereof; a light absorption film laminated on the fluorescent conversion film on the side of the display plane of the fluorescent conversion film; wherein the light absorbance of the fluorescent conversion film is 1 or less in the wavelength region between 450 nm and 520 nm; the light absorbance of the light absorption film is more than 1 in the wavelength region between 450 nm and 520 nm.
11. The colour display device according to Claim 10, wherein the fluorescent conversion film comprises a photo-curing resin as the matrix resin thereof.
12. The colour display device according to Claim 10, wherein the fluorescent conversion film comprises a photo- and thermo-setting resin as the matrix resin thereof.
13. The colour display device according to Claim 11, wherein the photo-curing resin contains an acrylate polymer as the main component thereof.
14. The colour display device according to Claim 11, wherein the photo-curing resin contains a methacrylate polymer as the main component thereof.
15. The colour display device according to Claim 11, wherein the photo-curing resin contains an acrylate-methacrylate copolymer as the main component thereof.
16. The colour display device according to Claim 12, wherein the photo- and thermo-setting resin contains an acrylate polymer as the main component thereof.
17. The colour display device according to Claim 12, wherein the photo- and thermo-setting resin contains a methacrylate polymer as the main component thereof.

18. The colour display device according to Claim 12, wherein the photo- and thermo-setting resin contains an acrylate-methacrylate copolymer as the main component thereof.
19. A fluorescent conversion filter substantially as described herein with reference to and as shown in the accompanying drawings.
20. A colour display device substantially as described herein and as shown in the accompanying drawings.



Application No: GB 9920733.4
Claims searched: 1-20

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Examiner: Emma Rendle
Date of search: 6 December 1999

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.Q): H1K (KEAL, KEAX)

Int Cl (Ed.6): H01L 33/00, 51/20; H05B 51/20

Other: EPOQUE: WPI, EPODOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0 861 016 A1 (IDEMITSU KOSAN) see whole document, especially colour changing layers 22 and page 4 lines 35-56.	1-18
X	EP 0 849 979 A2 (TDK) see whole document, especially figure 1 and page 3 lines 32-45.	1 and 10 at least

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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